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HYDROPHOBIC SOL-GEL COATINGS ON BIO-BASED MATERIALS – INFLUENCE OF CATALYST AND SOLVENT CONCENTRATION

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Abstract

The impact of depositing sol-gel coatings on the hydrophobicity of a bio-based material was investigated in this study. Bio-based materials have tendency to absorb large amounts of water due to their highly porous structure and presence of hydrophilic hydroxyl groups in their structure. For this purpose, two sets of silica sols were prepared to study the influence of catalysts and solvent concentration on the hydrophobicity of hemp shiv. The first set of silica sols were prepared using different acidic (hydrochloric acid and nitric acid) and basic (sodium hydroxide and ammonium hydroxide) catalysts while keeping the concentration of precursors and solvents constant. The hydrophobicity of sol-gel coated hemp shiv increased significantly when using acid catalysed sols resulting in water contact angles of up to 100° using sessile drop method.

Therefore, the next set of silica sols were prepared with acidic catalysts using higher concentration of solvent. Hemp shiv coated with ethanol diluted sols showed better hydrophobicity when compared to undiluted sols. This difference in hydrophobicity can be attributed to the change in surface roughness. It was found that silica sols containing higher concentration of solvent provide a uniform coating layer covering the hemp shiv entirely. In contrast, undiluted sol coatings developed minor cracks on the hemp shiv surface as observed under 3D optical profilometer. Therefore, the use of diluted hydrophobic silica sols offers potential for treatment of extremely hydrophilic bio-based materials by sol-gel technology. For practical application of coatings on bio-based materials, diluted silica sols are of interest due to longer shelf life, reduced cost and lower environmental impact of precursors.

Keywords:

Hemp shiv, Hydrophobicity, Roughness, Sol-gel, Catalyst, Solvent.

1 INTRODUCTION

The use of bio-based materials (derived from plant sources) have become increasingly popular to produce economical engineering materials in the construction industry [Faruk 2012]. Bio-based materials have numerous advantages over conventional non-renewable building materials such as lower embodied energy, lower CO2 emissions of buildings and demand for in-use energy can be significantly reduced through passive environmental control [Lawrence 2015]. Other advantages of bio-based materials include good specific strength, lower density, economic viability, biodegradability, non-irritant nature and good heat capacity [Dhakal 2007].

Bio-based materials are generally very porous with low density tending to absorb large amounts of water. Moreover, the presence of cellulose, hemicellulose and lignin in bio-based materials contributes to the presence of hydrophilic hydroxyl groups in their structure. This leads to certain disadvantages of using bio-based materials making them incompatible with hydrophobic thermoset/ thermoplastic polymers [Gassan 2000].

There is a high competition between the binders used with bio-based material due to the wide use of different binders in construction. Since the shiv competes with the binder for the available water, purely hydraulic binders like lime or cement cannot hydrate completely, leading to a powdery inner core in the hemp-lime walls which is poorly bound [Elfordy 2008]. During the manufacture of hemp concrete, water is added in significant excess amounts compared to what is needed for the hydration of lime. This leads to long drying times ranging from several months to over a year which are not acceptable to be implied at an industrial scale [Arnaud 2012].

Large water absorption capacity of bio-based materials can even cause problems in the end-product stage when undesirable water comes in contact or if the surroundings are humid. Previous studies have reported that hemp shiv not only has higher water absorption rate but also absorb high amounts of water in the very first minutes compared to different plant materials. [Kyma 2001].

Wettability of a solid surface is governed by a combination of chemical composition and geometric structure of the surface [Genzer 2006]. The interplay between surface chemistry and surface roughness has been an active research topic for enhancing the hydrophobicity of cellulose based materials. Plasma etching, lithography, electrospinning and sol-gel treatment are some techniques that endow the surface with nano-scale roughness [Song 2013].

The sol-gel technique is a highly versatile method to deposit silica based coatings possessing single or multi functionality [Brinker 1990]. These thin mesoporous coatings have high structural homogeneity and their adhesion can be tailored to different substrates. Sol-gel based hydrophobic and water repellent coatings have been investigated on different plant based materials such as wood and cellulosic fibres, however for hemp shiv this is the first time. The reactive hydroxyl groups in the polysiloxane network combine with the hydroxyl groups of cellulose forming a covalent bond.

This research focused on studying different catalysts for processing sol-gel coatings and determining the effect of these coatings on the hydrophobicity of hemp shiv. The impact of diluted sol-gel coatings on the surface roughness of the bio-based material has been investigated in this paper.

2 EXPERIMENTAL

2.1 Materials

Hemp shiv used in this study was received from MEM Inc., manufacturer of ecological materials based in Rimouski, Quebec. Tetraethyl orthosilicate (TEOS, 98%) and hexadecyltrimethoxysilane (HDTMS, 85%) were obtained from Sigma-Aldrich. Anhydrous ethanol was purchased form Commercial Alcohols, Canada. Hydrochloric acid (HCl, 38%), nitric acid (HNO3, 70%) sodium hydroxide (NaOH, 50%) and ammonium hydroxide (NH4OH, 28%) were obtained from Anachemia, VWR, Canada. All chemicals were used as received without further purification.

2.2 Preparation of the hydrophobic coatings

The silica based sol-gel was synthesised by hydrolysis and condensation of TEOS in ethanol and water. The reaction was catalysed by using either an acidic (HCl, HNO3) or basic (NaOH, NH4OH) catalyst in concentrations from 0.005M to 0.05M. Two sets of silica sols were prepared based on the difference in concentration of ethanol. The first set of sols (SOL A) were prepared stirring 1M TEOS in a mixture of 4M water and 4M ethanol. For the preparation of the second set of sols (SOL B), 1M TEOS was added to 4M water and 16M ethanol. After the preparation of both silica sols the hydrophobic agent HDTMS was added in concentrations of 4 wt% of the sol. These mixtures of silica sol and HDTMS were stirred for at least 20 minutes before performing the dip-coating process. All the sols prepared are listed in Table 1.

Gelation took place in-situ in which pieces of hemp shiv were dipped in the sol for 10 min and then carefully removed and transferred onto a Petri dish. The samples were placed at room temperature for one hour and then dried at 80 °C for one hour.

For preparation of the pure sol-gel, the sol was allowed to age in a container at room temperature until gel point. The gel-point was taken as the time when the sol did not show any movement on turning the container upside down. The gel-time for the sols are reported in Table 1.

2.3 Characterisation techniques

Contact Angle Measurements: The water contact angle (WCA) of uncoated and coated hemp shiv samples were measured using a contact angle meter (First Ten Ångstroms USA, FTA200 series. The sessile drop method was employed and the contact angle was determined on at least three different positions for each sample. The average value was adopted as a final value. Images were captured and analysed using the FTA32 Video 2.0 software. All the measurements were performed at room temperature (24 ± 1 ◦C).

Surface Characterisation: The topography and surface roughness of the samples was obtained using a 3D optical profilometer (Bruker Nano GmbH Germany, ContourGT-K series). The surface roughness were measured over an area at 0.25*0.30 mm2 in non-contact mode at 20X magnification. Vision 64 onboard software was then employed to analyze these data and calculate the roughness parameters. The readings were taken on at least three different positions for each sample and the average value was reported as the final value.

Tab. 1: Sol compositions and gel-time.

SOL	CATALYST	CONCENTRATION (M)	GEL TIME (DAYS)
SOL A-1	HCl	0.005	178
SOL A-2	HNO_3	0.005	150
SOL A-3	NaOH	0.05	6
SOL A-4	NH_4OH	0.05	5
SOL B-1	HCl	0.005	>180
SOL-B-2	HNO_3	0.005	>180

3 RESULTS AND DISCUSSION

3.1 Hydrophobicity of sol-gel coatings

Among the coating compositions listed in Table 1, the coatings prepared using acidic catalysts showed better contact angles. From Figure 1, it can be seen that uncoated shiv has an extremely hydrophilic surface and water droplet sinks into the substrate reducing the WCA in short time. The sol-gel coatings tend to reduce the hydrophilicity of the hemp shiv by maintaining a stable contact angle over 60 seconds. However, it is clear that using this process of sol-gel dip coating, the basic sols are unable to provide a hydrophobic surface (WCA<90°) on the hemp shiv.

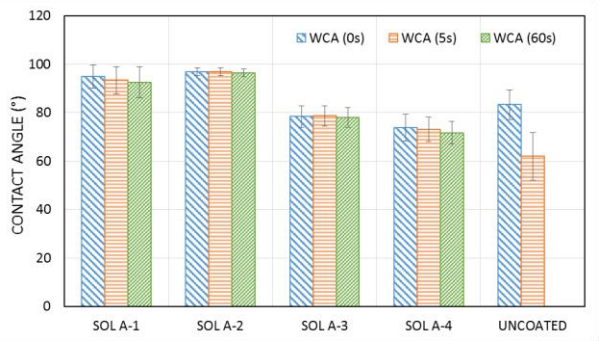

Fig. 1: Water contact angle (WCA) of uncoated and sol-gel coated hemp shiv for 0-60 seconds of contact.

It is well known that the in the sol-gel process, basic sols result in the production of silica nanoparticles. Cellulose based fibres can be covered by silica nanoparticles by simple dip coating [Zhou 2013], by spraying SiO2 nanoparticles suspended in alcohol [Ogihara 2012] or by heat treatment [Xu 2011] resulting in a chemical bond formation between silica and the hydroxyl groups of cellulose.

Silica nanoparticles prepared by the sol-gel process are usually negatively charged and the surface of cellulose fiber carries negative charges in aqueous solution as well. Therefore, the coverage of silica nanoparticles on cellulose based fibers without pre-treatment is quite poor [Bae 2009, Yu 2007], which may affect the strength of the functionality it is expected to provide on the material. This may be the reason for the lower WCA on hemp shiv coated with basic sols. In order to enhance the hydrophobic functionality, the nanoparticle coverage and roughness needs to be increased. This can be obtained by depositing multilayers of silica nanoparticles and combining the basic sol-gel suspension with cationic polyelectrolytes [Song 2013].

The acidic sols (SOL A-1 and SOL A-2) enhance the water repellence of hemp shiv making the surface hydrophobic (WCA>90°). Sols prepared using acid catalysts are deposited as continuous thin membranes rather than nanoparticles. The contact angle for hemp shiv coated with SOL A-2 remains stable for up to three minutes (data not shown in figure 1) while the contact angle for SOL A-1 coatings decrease slightly with time. This will be discussed in the next section.

Acidic sol coatings with varying solvent concentrations were applied on hemp shiv and the WCA readings are reported in Figure 2. It was observed that diluted sols (SOL B) having higher concentration of ethanol perform better in terms of providing hydrophobicity to hemp shiv samples.

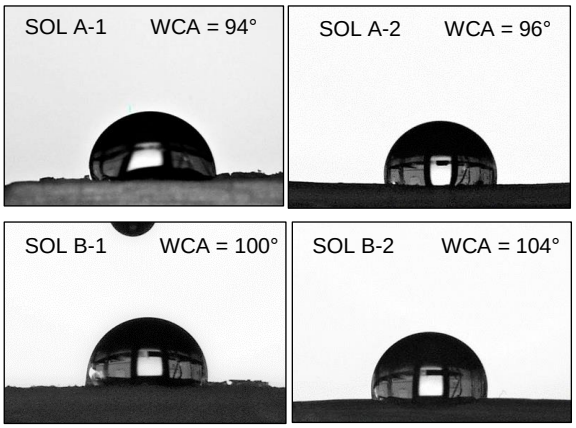

Fig. 2: WCA measurements on hemp shiv with different sol-gel coatings.

3.2 Surface microstructure of the coatings

The surface roughness of the samples was analysed by the Vision64 software using a Robust Gaussian Filter (ISO 16610-31 2016) and a short wavelength cutoff of 0.025mm. The robust Gaussian filter avoids the distortions produced by some filters when applied in profiles with deep valleys [Ugulino 2016]. Mean surface roughness (Sa), root-mean square roughness (Sq), maximum height of peaks (Sp), maximum depth of valleys (Sv) and ten points height of the surface (Sz) were calculated according to ISO 4287 (1997). The roughness parameters are listed in Table 2 for all the samples coated with acidic sol-gel.

Tab. 2: Surface roughness parameters of hemp shiv with different sol-gel coatings.

Sample	Sa (µm)	Sq (µm)	Sp (µm)	Sv (µm)	Sz (µm)
Uncoated	1.47	2.21	7.30	-22.30	29.60
SOL A-1	1.17	2.18	4.24	-42.55	46.79
SOL A-2	1.14	1.92	4.96	-33.48	38.45
SOL B-1	2.39	3.35	17.33	-31.50	48.83
SOL-B-2	2.31	3.61	14.79	-35.96	50.75

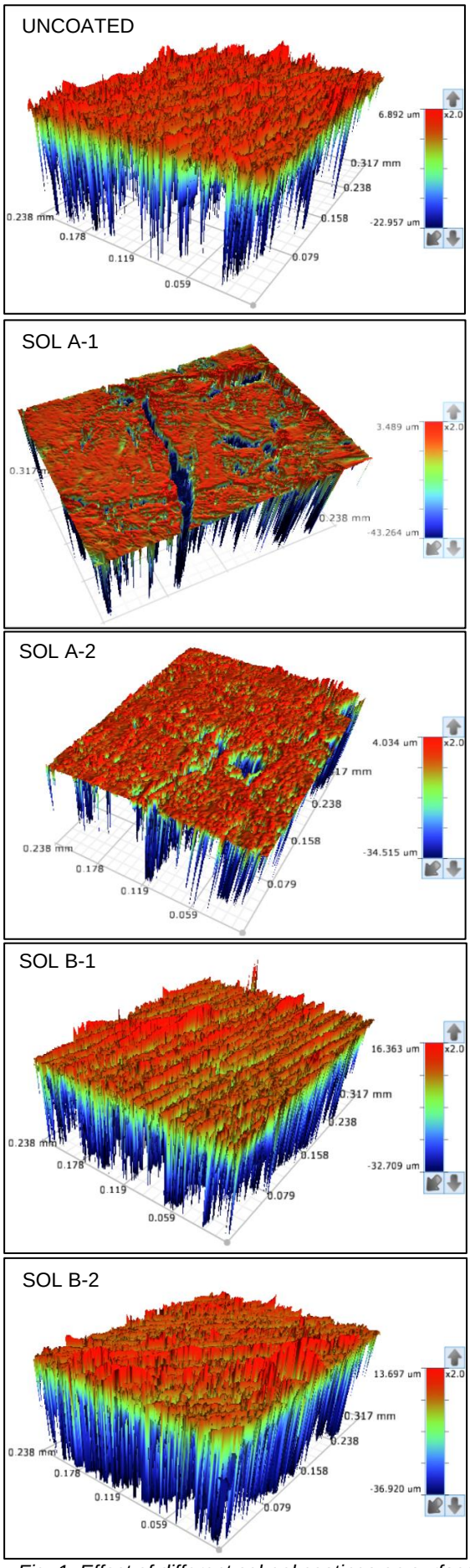

Fig. 1: Effect of different sol-gel coatings on surface morphology of hemp shiv.

The surface roughness of hemp shiv is altered after coating with sol-gel as seen in Figure 3. Hemp shiv coated with SOL A-1 and SOL A-2 show a smoother surface when compared to the uncoated shiv. However, it was observed that SOL B-1 and SOL B-2 increase the surface roughness of the hemp shiv which is thought to be reason for higher contact angles as seen in Figure 2. Moreover, it can be seen from Figure 3, that SOL A-1 coated shiv develop cracks on the surface and SOL A-2 coatings are not uniform. This is an important factor to be considered as the long-term water absorption can be affected by the presence of cracks on the hydrophobic surface.

4 SUMMARY

The effect of depositing hydrophobic sol-gel coatings with acidic and basic catalysts on hemp shiv were investigated. Basic sol-gel coatings did not provide hydrophobicity to the substrate, although it enhanced the water-repellence of the hemp shiv maintaining a stable contact angle. Sol-gel coatings with acidic catalysts show promising results for providing a hydrophobic surface. The presence of higher solvent concentration in the acidic sol showed better results for WCA and enhanced the surface roughness of hemp shiv. It can be concluded that acidic sol-gel coatings diluted with ethanol would be of interest in the industry for coating extremely hydrophilic bio-based materials due to their long shelf life, reduced cost and lower environmental impact of silanes. Moreover, the presence of higher organic solvent content would result in shorter drying time and lower curing temperature thereby reducing the energy consumption.

5 ACKNOWLEDGMENTS

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6 REFERENCES

Arnaud, L.; Gourlay, E.; Experimental study of parameters influencing mechanical properties of hemp concretes. Construction and Building Materials, 2012, 28, 1, (50–56), doi:10.1016/j.conbuildmat.2011.07.052.

Bae, G. Y.; Min, B. G.; Jeong, Y. G.; Lee, S. C.; Jang, J. H.; Koo, G. H.; Superhydrophobicity of cotton fabrics treated with silica nanoparticles and water-repellent agent. Journal of Colloid and Interface Science, 2009, 337, 1, (170–175), doi:10.1016/j.jcis.2009.04.066.

C. Brinker; Scherer, G.; Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing. Advanced Materials, 1990 doi:10.1186/1471-2105-8-444.

Dhakal, H. N.; Zhang, Z. Y.; Richardson, M. O. W.; Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester

composites. Composites Science and Technology, 2007, 67, 7–8, (1674–1683), doi:10.1016/j.compscitech.2006.06.019.

Elfordy, S.; Lucas, F.; Tancret, F.; Scudeller, Y.; Goudet, L.; Mechanical and thermal properties of lime and hemp concrete (“hempcrete”) manufactured by a projection process. Construction and Building Materials, 2008, 22, 10, (2116–2123), doi:10.1016/j.conbuildmat.2007.07.016.

Faruk, O.; Bledzki, A. K.; Fink, H. P.; Sain, M.; Biocomposites reinforced with natural fibers: 2000-2010. Progress in Polymer Science, 2012, 37, 11, (1552–1596), doi:10.1016/j.progpolymsci.2012.04.003.

Gassan, J.; Gutowski, V. S.; Bledzki, A. K.; About the surface characteristics of natural fibres. Surface Engineering, 2000, 283, 1, (132–139).

Genzer, J.; Efimenko, K.; Recent developments in superhydrophobic surfaces and their relevance to marine fouling: a review. Biofouling, 2006, 22, 5–6, (339–360), doi:10.1080/08927010600980223.

Kyma, H.; Hautala, M.; Kuisma, R.; Pasila, A.; Capillarity of flax / linseed (Linum usitatissimum L .) and fibre hemp (Cannabis sati 6 a L .) straw fractions. 2001, 14, (41–50).

Lawrence, M.; Reducing the Environmental Impact of Construction by Using Renewable Materials. Journal of Renewable Materials, 2015, 3, 3, (163–174), doi:10.7569/JRM.2015.634105.

Ogihara, H.; Xie, J.; Okagaki, J.; Saji, T.; Simple method for preparing superhydrophobic paper: Spray-deposited hydrophobic silica nanoparticle coatings exhibit high water-repellency and transparency. Langmuir, 2012, 28, 10, (4605–4608), doi:10.1021/la204492q.

Song, J.; Rojas, O. J.; Approaching super-hydrophobicity from cellulosic materials: A Review. Paper Chemistry, 2013, 28, 2, (216–238), doi:10.3183/NPPRJ-2013-28-02-p216-238.

Ugulino, B.; Hernández, R. E.; Assessment of surface properties and solvent-borne coating performance of red oak wood produced by peripheral planning. European Journal of Wood and Wood Products, 2016, (1–13), doi:10.1007/s00107-016-1090-6.

Xu, L.; Zhuang, W.; Xu, B.; Cai, Z.; Fabrication of superhydrophobic cotton fabrics by silica hydrosol and hydrophobization. Applied Surface Science, 2011, 257, 13, (5491–5498), doi:10.1016/j.apsusc.2010.12.116.

Yu, M.; Gu, G.; Meng, W. D.; Qing, F. L.; Superhydrophobic cotton fabric coating based on a complex layer of silica nanoparticles and perfluorooctylated quaternary ammonium silane coupling agent. Applied Surface Science, 2007, 253, 7, (3669–3673), doi:10.1016/j.apsusc.2006.07.086.

Zhou, H.; Wang, H.; Niu, H.; Gestos, A.; Lin, T.; Robust, self-healing superamphiphobic fabrics prepared by two-step coating of fluoro-containing polymer, fluoroalkyl silane, and modified silica nanoparticles. Advanced Functional Materials, 2013, 23, 13, (1664–1670), doi:10.1002/adfm.201202030.